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Titanium dioxide induced failure in polycarbonate

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Incorporation of low levels of fillers into thermoplastics can often lead to an increase in the modulus and a general improvement in the mechanical properties. However, increasing the level of filler loading can lead to a dramatic loss of impact strength and related mechanical properties. In this study the pigmentation of polycarbonate (PC) with titanium dioxide (TiO_2) is shown to lead to a reduction in the fracture energy and changes in the failure mechanism of injection moulded test samples. Electron microscopic examination of the fracture surfaces indicates that changes in the failure mechanism are a result of the occurrence of large areas of densified polymer around pigment particles. Densification reduces the extent of segmental motion within the polymer matrix, as indicated by dielectric and thermally stimulated discharge current measurements. The influence on the molecular motion and mechanical properties of the degree of drying, molecular weight of the polymer and concentration of TiO_2 are reported. Complementary positron annihilation measurements allow a tentative mechanism to be proposed to explain the loss of impact strength in these materials. Data is also presented on polybutylene terephthalate (PBT) pigmented materials and a PC system in which the TiO_2 has been mixed with polyethylene prior to dispersion in the PC matrix. These observations confirm the importance of polymer–pigment interactions in determining the fracture properties of samples.

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1. Introduction

The fracture energy of a thermoplastic polymer is directly related to the energy dissipated in the region of crack growth [1]. Pigmentation of a thermoplastic can cause polymer molecules to be absorbed onto the surface and this in turn can lead to regions of densification. If, however, there is no absorption, the filler particles disrupt the polymer matrix and lead to a more open structure. In the latter case there is a plasticization effect and in the former an antiplasticization effect [1–3]. Closer packing of polymer molecules results in a reduction in the available free volume for segmental motion and can lead to an increase in the glass transition temperature, T_g, as well as a reduction in sub T_g processes [2]. In PC the effect of pigment incorporation has a sensational effect on the mechanical properties, even at low levels. The dramatic loss of impact strength is a major barrier to the application of pigmented PC. Polycarbonate possesses a large free volume at room temperature and this in part explains the high impact strength observed for the pure material. However, Vollenberg *et al.* [4] propose that densification of PC leads to an increase in Young's modulus and a consequent reduction in the fracture toughness. As the impact strength can be correlated with the ability of polymer chains to execute segmental motion and hence dissipate the energy associated with crack growth propagation [5–7], any densification which causes a reduction in free volume will reduce segmental motion and thus the associated mechanical properties.

Segmental motion has been the subject of extensive investigations using dielectric, mechanical and nuclear magnetic resonance measurements. These techniques have shown that the sub T_g processes in PC involve rotation of the carbonyl dipole coupled with librational motions of the phenyl rings [8–15]. In this paper a study of mechanical and polar properties is presented, as well as positron annihilation and electron microscopy, in an attempt to clarify the molecular origins of the loss of mechanical properties in pigmented PC.

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2. Experimental procedure

2.1. Materials

Two types of PC were used in this study; a general purpose grade material obtained from Whitfield Ltd, Leeds (PCD), and a narrow molecular weight distribution sample obtained from Dow Chemicals BV (PCA). The latter is a research grade material, similar to Calibre 31, but is not generally available commercially. The molecular weight characteristics of the polymers were measured by gel permeation chromatography (GPC), Table I.

The pigment used was a fine rutile crystal grade TiO_2. After dry tumbling with PC the blend was dried at 393 K for a minimum of 4 h, prior to extrusion. Two extruders were used; a Betal 30 mm single screw and a Leistritz 35 mm twin screw extruder with a length to diameter ratio of 31:1. Following drying at the same temperature for a further 2–4 h, the granulated material was injection moulded to provide a dumbbell for tensile testing, a bar for impact measurements and a square plaque for polymer characterization. A range of samples were prepared using pigment which had been previously dried at 423, 473, 523 and 573 K prior to the tumbling process. GPC analysis of samples of the final compounded material dissolved in tetrahydrofuran (THF) and filtered indicated that processing had a minimal effect on molecular weight.

2.2. Injection moulding procedure

Injection moulding of the samples was carried out using a Peco limited model number 15MR which uses a 40 g shot capacity reciprocal screw type operation. The PC was moulded using a cylinder temperature of 453 K and a mould temperature of 393 K. The first ten samples generated during each processing run were rejected.

2.3. Assessment of dispersion by contact microradiography

The degree of dispersion of the pigment in the polymer matrix was determined using contact microradiography (CMR). The extruded material was pressed into a flat slab and then laid on top of a photographic plate and exposed to an X-ray source. The X-rays passed directly through the amorphous polymer matrix, but were absorbed or diffracted by the crystalline pigment. On development of the photographic plates, any black unexposed areas indicate the presence of an agglomerate of TiO_2. This allows a qualitative estimate of the degree of dispersion which is achieved during extrusion. As expected the twin screw extruder achieved a more satisfactory dispersion of pigment than the single screw extruder. As a consequence, the data presented in this paper was obtained using the twin screw extruded material.

TABLE I Molecular weight characteristics of the polycarbonates used in this study

Sample	M_w	M_n	M_w/M_n
PCD	2.4×10^4	2.1×10^4	1.14
PCA	1.9×10^4	1.4×10^4	1.36

2.4. Mechanical testing

Two types of measurements were performed on the samples

1. Tensile testing: stress–strain curves were measured for the samples using a Monsanto 500 tensometer. The modulus was determined from the initial slopes, fracture toughness was calculated from the area under the stress–strain curve and the ultimate tensile strength and the elongation to break were determined from the failure point.

2. Impact test measurements: these measurements were carried out using a Losenhausen Charpy impact tester for the lightly pigmented samples of PC and an Avery impact tester for the PBT and the weaker materials. Both devices utilize a pivoted hammer and are normally operated in the rear anvil mode. The sample used was 60 mm long, 3 mm thick, 10 mm wide and "V" notched to a depth of 3 mm.

2.5. Thermally stimulated discharge current (TSD) measurements

Thermally stimulated discharge current (TSD) measurements have been used by van Turnhout and others for the study of the dipolar motion in polymeric materials [16–19]. The apparatus used in this study is described elsewhere [20]. The technique investigates the discharge obtained on thermally scanning an electret generated on poling the sample at high temperature followed by quenching. The measurements were performed using a 6.25 cm^2, silver coated square plaque, cut from the injection moulded square.

2.6. Positronium lifetime measurements

Positronium lifetime measurements for certain samples was obtained using a fast/slow positron annihilation spectrometer (PAL). The apparatus has been described elsewhere [21]. Two PC samples were cut from the moulded plaque and placed either side of an Na^{22} positron source. This assembly was placed in a glass tube and thermostatted in an Oxford Instruments DN704 cryostat. The temperature was controlled with a precision of ± 0.1 K in the range 300–400 K using an Oxford Instruments DTC2 temperature controller. The collected data was analysed using a computer program called POSITRONFIT [22]. The apparatus having been already characterized using a benzophenone standard and RESOLUTION [23], a program designed to characterize the apparatus.

2.7. Differential scanning calorimetry (DSC)

DSC analysis was carried out on the moulded polymer materials using a DuPont 9900 thermal analyser system. The analysis of the PBT materials was carried out using a Perkin Elmer DSC7. The glass transition temperature of PC and the freezing point of PBT were recorded.

2.8. Dielectric measurements

Dielectric measurements were carried out using a network analyser to produce frequencies between 6×10^5 and 10^{-3} Hz. This signal was then applied over the sample and a balanced air capacitor. The response was recorded using a frequency response analyser. The apparatus has been described in detail elsewhere [24]. The sample was cut from the square plaque and silver coated. The sample was then thermostatted between 160 and 300 K to the precision of ± 0.1 K in an Oxford Instruments DN704 cryostat.

2.9. Electron microscopy

Electron micrographs were taken of the fracture surfaces using a Philips scanning electron microscope (SEM) fitted with an energy dispersive X-ray analyser (EDAX). The samples were rendered conductive by evaporating a thin covering of gold onto the surface prior to being placed in the beam chamber.

3. Results and discussion

3.1. Mechanical testing

3.1.1. Tensile measurements

The stress–strain curves obtained from the materials fall into one of two distinct classes, as illustrated in Fig. 1a,b. Fig. 1a, is typical of a material demonstrating a ductile failure process, while in Fig. 1b, the fracture process is defined as a brittle type mechanism. Each of the materials tested in this study could easily be placed into one of these categories.

Initially one felt that the reported degradation in the impact properties of PC was perhaps related to the influence of water present during processing. In order to investigate this the authors undertook an extensive study of varying levels of drying conditions. Initially a set of samples was produced without any predrying whatsoever. The tensile test results for the undried materials are shown in Fig. 2a,b. The yield strength of the material initially increases with increasing levels of TiO_2. Whereas the ultimate tensile strength shows a marked decrease with a loading above 0.5% TiO_2. The values of both the yield strength and ultimate tensile strength for the unpigmented material are somewhat lower than those that would normally be expected for this grade of PC.

In the next set of samples the materials were dried at 393 K for 4 h prior to both extrusion and then again before injection moulding. The data obtained for these samples is shown in Fig. 3a,b. The yield strength of the dried samples was significantly higher than the undried samples: 47 N-mm^{-2} for the undried compared with 57 N-mm^{-2} for the PCD and 50.5 N-mm^{-2} for the PCA. This result illustrates the effect of water incorporated within the polymer prior to processing and portrays the need to adequately dry the polymer before processing.

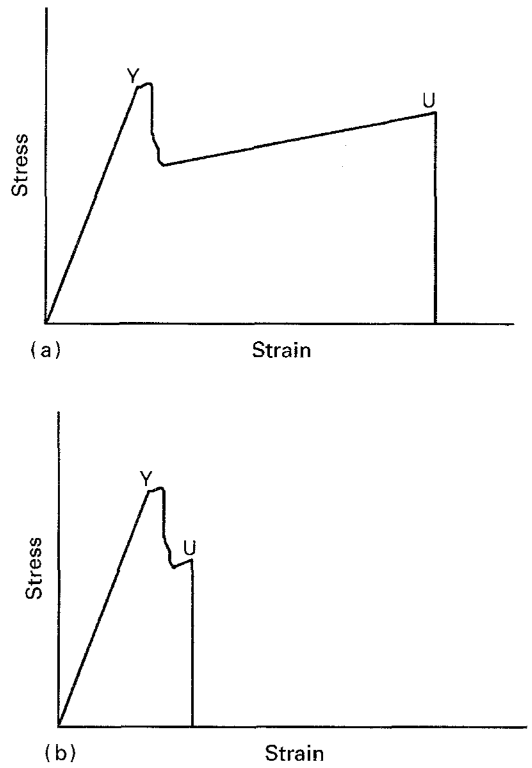

Figure 1 Typical stress–strain response for (a) ductile behaviour and (b) brittle behaviour, showing yield point, *Y*, and ultimate tensile strength, *U*.

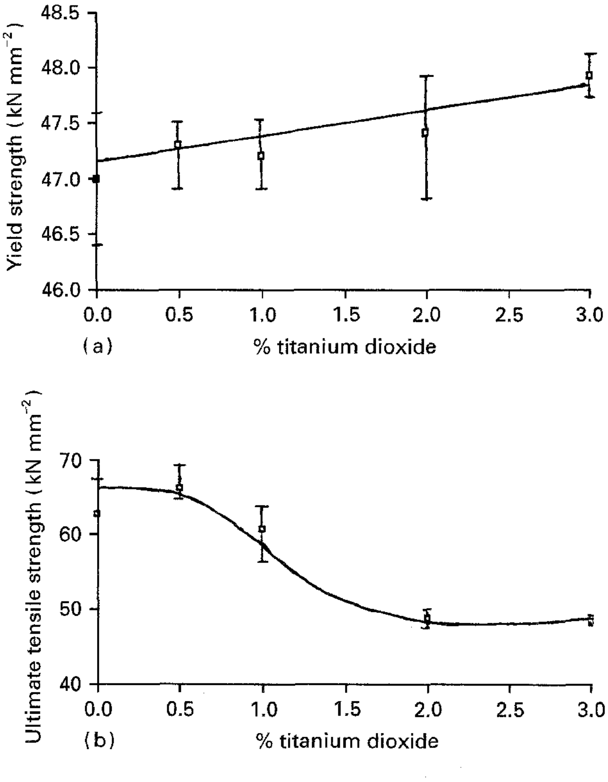

Figure 2 Mechanical properties of undried PCD: (a) Upper yield strength and (b) ultimate tensile strength.

Secondly, the effect of further drying the pigment was investigated. The pigment was predried at temperatures of 423, 473, 523 and 573 K before dry tumbling with the polymer and further drying at 293 K for 4 h prior to processing. The mechanical properties of these materials is summarized in Fig. 4a,b. The yield

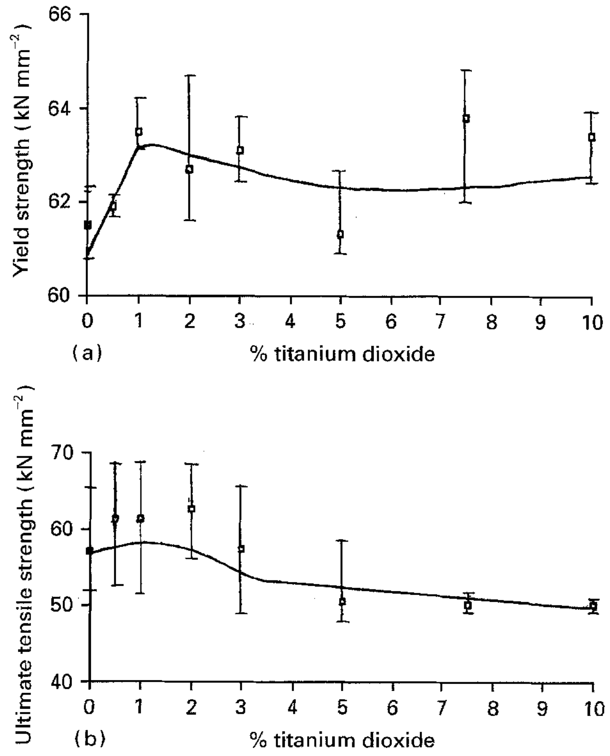

Figure 3 Mechanical properties of PCD dried at 393 K for 4 h. (a) upper yield strength and (b) ultimate tensile strength.

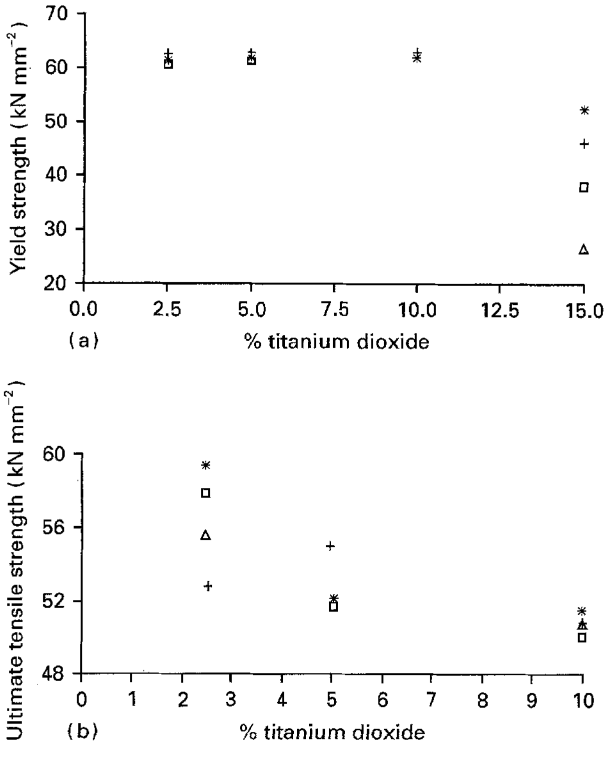

Figure 4 Mechanical properties of low molecular weight PCA, dried at 393 K for 4 H. (a) upper yield strength and (b) ultimate tensile strength dried at (□) 423 K, (+) 473 K, (*) 523 K and (Δ) 573 K.

strength of these materials is essentially insensitive to pigment drying conditions up to approximately 10% of filler, above that it shows a sensitivity to drying conditions, which cannot totally be explained in terms of water desorption from the surface of the pigment into the polymer during the moulding process. If water were to be desorbed from the pigment it would be expected that, as the drying temperature of the pigment was increased. so a comparable increase in the yield strength would be observed, consistent with the data presented in Fig. 4a, for the trend from 423 to 523 K. However, the marked decrease in the yield strength for the samples made with pigment dried at 573 K is inexplicable and raises doubts about this simplistic interpretation of the data. Similar examination of the ultimate tensile strength data further illustrates the shortcomings of this interpretation, as exemplified by the trends observed at 2.5% loading.

3.1.2 Investigations on polybutylene, terephthalate (PBT)

Titanium dioxide is a highly surface active filler and it is possible that the changes in mechanical behaviour may, in some part, be attributed to specific interactions between the surface and PC. In order to explore the specificity of the variations reported above, a comparative study was carried out with PBT. Polycarbonate has a backbone structure (–O–CO–O–R–), whereas the polyester structure can be represented (–O–CO–R–). Although these are intrinsically similar structures both containing carbonyl groupings, the flexibility and polarity of the carbonyls will be different in the two cases. The incorporation of the butyl group will significantly influence the flexibility of the chain and the ability of the carbonyl to undergo interaction with the filler surface. Mechanical measurements were carried out on a similar set of samples dried using comparable conditions. Once more the pattern of behaviour is repeated, Fig. 5a,b, the yield strength increasing modestly with increasing pigment level. However, in this case the ultimate tensile strength, Fig. 5b, fell off so rapidly, that in fact, above 3% it was no longer measurable. It may be concluded that there is a chemical effect and that the PBT, with its greater ability to interact with the pigment surface, is showing a more dramatic loss in ultimate tensile strength than the PC samples.

3.1.3. Ductile–brittle failure

It should be pointed out that the error bars indicated in the diagrams represent the actual variance in the test data, but on examination of the failed samples it is possible to divide these into two groups; the one set exhibiting ductile and the other brittle failure. Although caution has to be used when interpreting stress-strain curves, as microvoids and other surface defects can play a dominant effect in determining the nature of failure, when the test specimens were examined and a histogram of failure mechanism produced, Fig. 6, an interesting pattern emerged. One can see that, for all the systems measured in this study, the general pattern with increasing pigment level is for a shift from ductile to brittle failure. The pure unpigmented polymers, as expected, fail in a ductile fashion, whereas incorporation of pigment leads to an increasing probability of brittle failure. The variance in the values presented in the previous figures, therefore to some extent, represents the statistical distribution of

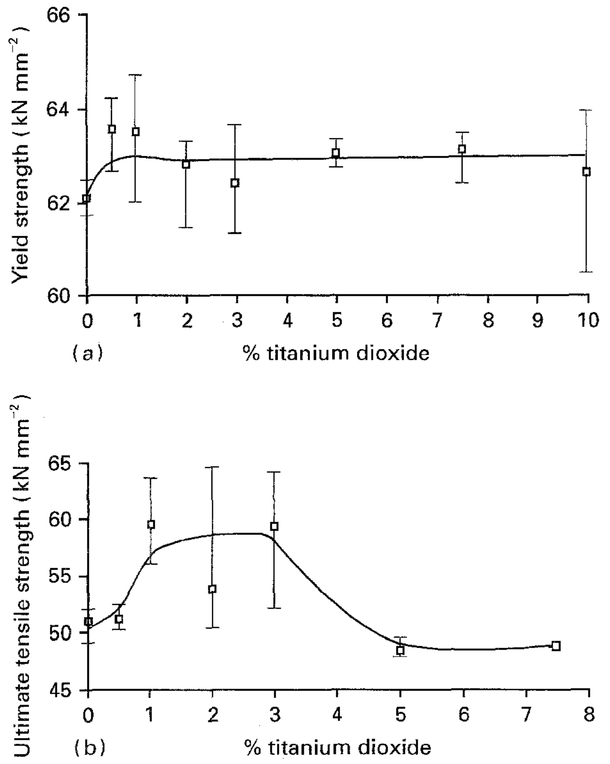

Figure 5 Mechanical properties of PBT, dried at 393 K for 4 h. (a) upper yield strength and (b) ultimate tensile strength.

the two failure mechanisms. Using the failure mechanism as a method of classifying samples, it is now possible to investigate percentage elongation to break for the ductile and brittle samples. Fig. 7 indicates the behaviour of each sample of PCD investigated and one sees that using the failure mechanism, one can divide the mechanical data into two distinct groups. One finds that a small incorporation of TiO_2 tends to enhance the level of elongation in ductile failure before break. However, in all cases the elongation associated with brittle failure is significantly lower than that for ductile processes in comparable samples.

3.1.4. *Influence of polymer surface interactions*

In an attempt to explore the possibility of the specific interactions between the polymer and the TiO_2 surface, a set of materials was generated by first encapsulating the TiO_2 with polyethylene (PE): this material, which was 50% weight/weight of pigment and PE, was used as a master batch and mixed with 80% PC prior to extruding. Mechanical data on these samples are presented in Table II. The master batch was generated by melt blending the PE with the pigment. Two control samples were generated, one with no pigment and a similar level of PE and where the PE and pigment were just dry mixed. It may, therefore, be assumed that the pigment would not be encapsulated by the PE. The results produced for these materials are not sufficiently different to be definitive. However, it is important to note that in all cases the material failed via a brittle fracture mechanism. The encapsulated pigment produced a slightly lower yield strength, than when the components were simply

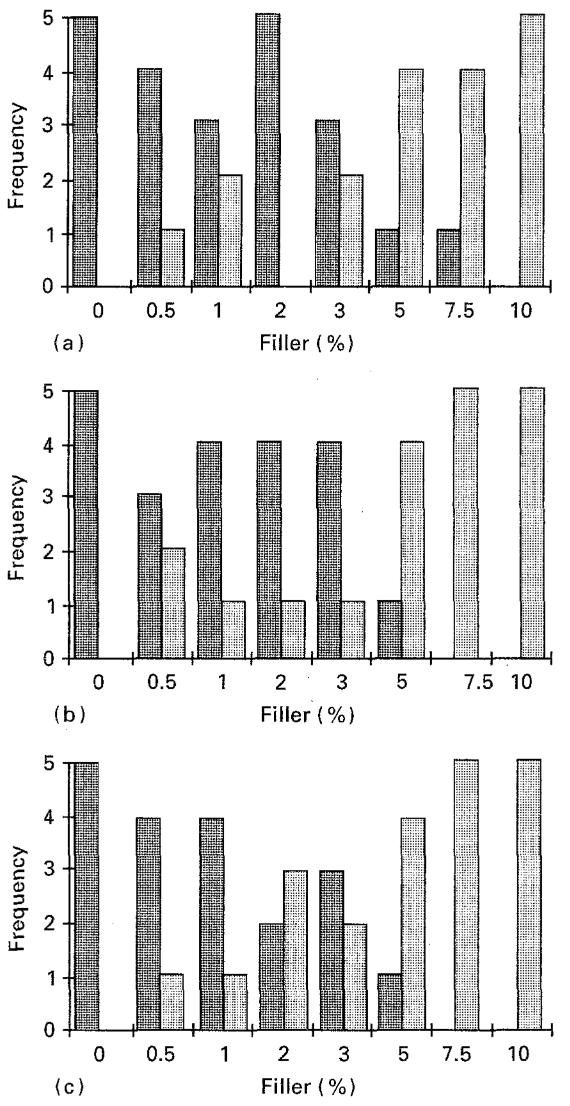

Figure 6 Histogram illustrating the distribution between (▨) ductile and (▦) brittle failures in the mechanical tests of dried PCD (a), dried PCA (b) and dried PBT (c).

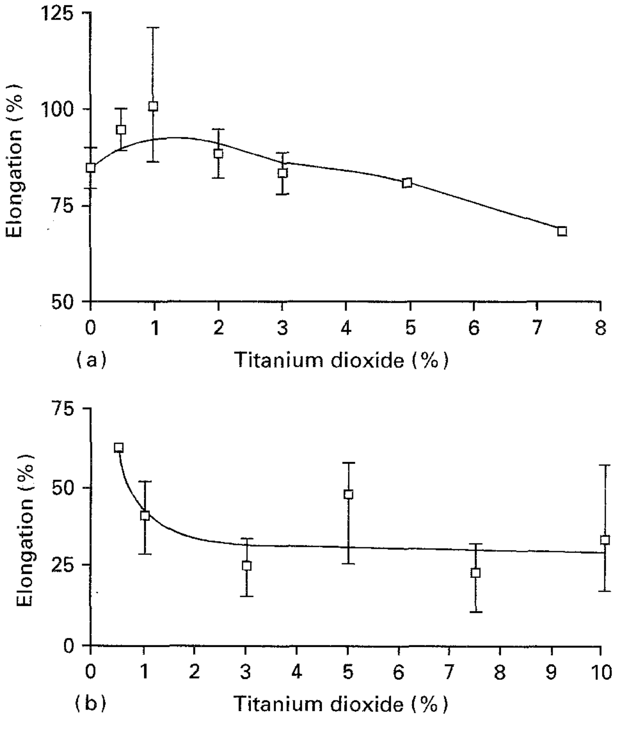

Figure 7 Elongation to break for PCD, (a) ductile mechanism and (b) brittle mechanism.

TABLE II Mechanical properties of PE loaded polycarbonates

Sample	Yield strength ($kN\,mm^{-2}$)	Fracture type	Impact strength (J)	Fracture type
PC/PE blend	44.59	Brittle	1.6	Ductile
PC/20% MB[a]	44.85	Brittle	1.6	Ductile
PC/PE/10%TiO_2	50.07	Brittle	1.2	Ductile

[a]MB, 1:1 premixed PE and TiO_2.

mixed together. A further important point to note is that even the sample which contained no pigment still exhibited a brittle fracture type mechanism. This would seem to suggest that the nature of the filler material does not affect the fracture mechanism, but is simply a consequence of the physical presence of filler material within the polymer matrix, whether that be PE or TiO_2 crystals.

3.1.5. Impact strength measurements

Notched impact measurements were carried out on the samples and typically these exhibited two types of failure mechanism, (Figs. 8, 9). Materials exhibiting a high impact strength failed by ductile process, (Fig. 8), indicating a plastic deformation in the region of the notch. The materials exhibiting low impact strengths tended to fail by brittle fracture (Fig. 9). Once more, a histogram of the frequency of failure for the various materials can be generated and that is shown in Fig. 10. As in the case of the stress–strain samples, the impact samples showed a similar dependence on a change in the failure mechanism with increasing pigment content. The initial materials all exhibited ductile fracture, whereas increasing the pigment content led to an increasing predominance of brittle fracture at high levels of filler content. The variation of the impact strength with the filler content for PCD and PCA samples failing via brittle or ductile fracture is presented in Fig. 11a, b. It can be seen that those samples failing via a ductile fracture exhibit significantly higher values than those failing via brittle fracture. The observed fall-off in terms of the impact properties of these materials may be ascribed to a greater statistical preponderance of the material to fail via a brittle fracture mechanism rather than by a ductile fracture mechanism. The lower values observed for the lower molecular weight PC may be ascribed to the fact that, in this latter material, the lower molecular weight of the polymer will lead to a lower degree of interchain entanglement and, hence, may lead to a greater densification of the polymer chains with a consequent restriction in the chain motion, resulting in a reduction in impact strength. The materials coated with PE were also investigated and the results are presented in Table III. Once again the encapsulation of a pigment in polyethylene did not affect the impact strength compared with the dry mixed material. There is a large reduction in the impact strength of the material containing only PE compared with the pure PC, 1.6 J compared with 3.0 J. This again indicates that a drop in the impact strength properties is caused simply by the physical presence of a filler material and is not specific to the incorporation of TiO_2. It is, however, interesting to note that in this case all the materials failed by a ductile process.

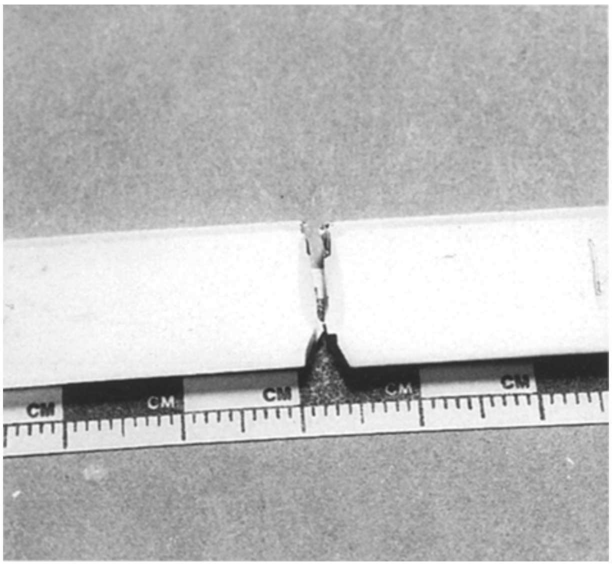

Figure 8 Ductile failure impact test bar.

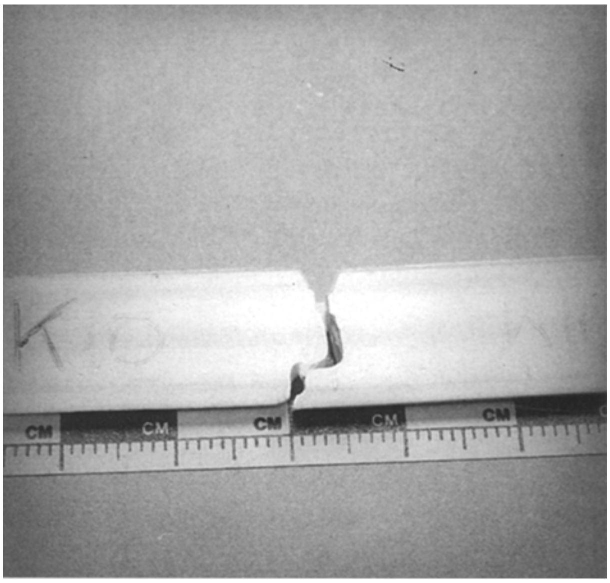

Figure 9 Brittle failure impact test bar.

3.2. Electron microscopic examination

In order to obtain a better understanding of the processes occurring during the failure of these samples,

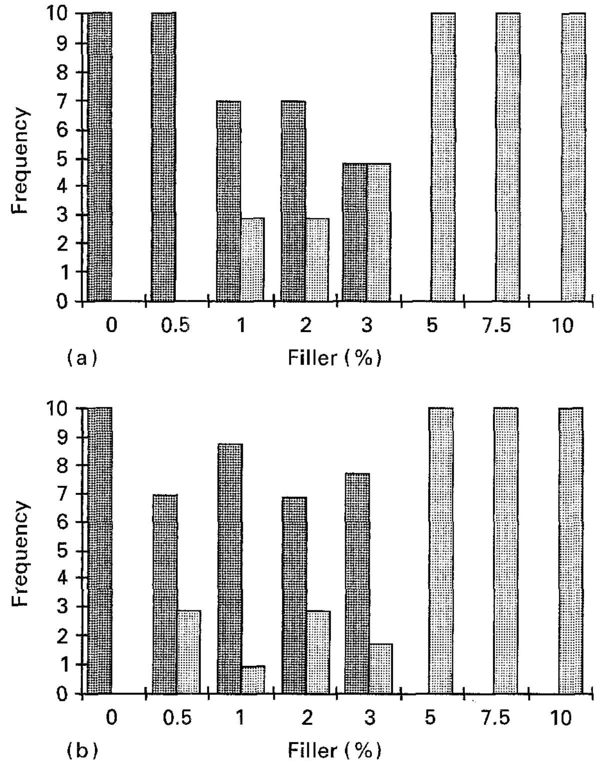

Figure 10 Histogram illustrating the distribution of (▨) ductile and (▦) brittle failures in the impact tests of dried PCD (a), dried PCA (b).

SEM investigations combined with an energy dispersive X-ray analysis (EDX) was carried out on the fracture surfaces. The brittle fracture material showed areas of apparent densification around the notch edge (Fig. 12). These areas of densification appear as circular crater-like areas in the SEM photographs. EDX analysis of these areas showed an extremely high concentration of titanium dioxide at the centre of the crater. Ductile failure showed a typical tear texture across the surface (Fig. 13). In the brittle failure materials densified regions promote fast crack growth with little energy dissipation, thus resulting in a low impact strength and no deformation. However, in the ductile failures the lack of these regions prevents rapid crack growth and results in a slow tearing type mechanism, which leads to large absorption of energy giving high impact strengths and large areas of deformation. From these results one may conclude that the changes in the fracture process must be related to the appearance of these densified regions within the material.

Although orientation of PC chains has been observed under high strain [25, 26] and some models have been developed to describe this type of orientation in otherwise amorphous materials [27, 28], the three-dimensional appearance of the densified regions suggest that these are not formed from the application of a tensile load, but are generated during the processing of the material. It may be proposed that the incorporation of filler material, either TiO_2 or PE, leads to a site of nucleation for the growth of a "densified form" of PC.

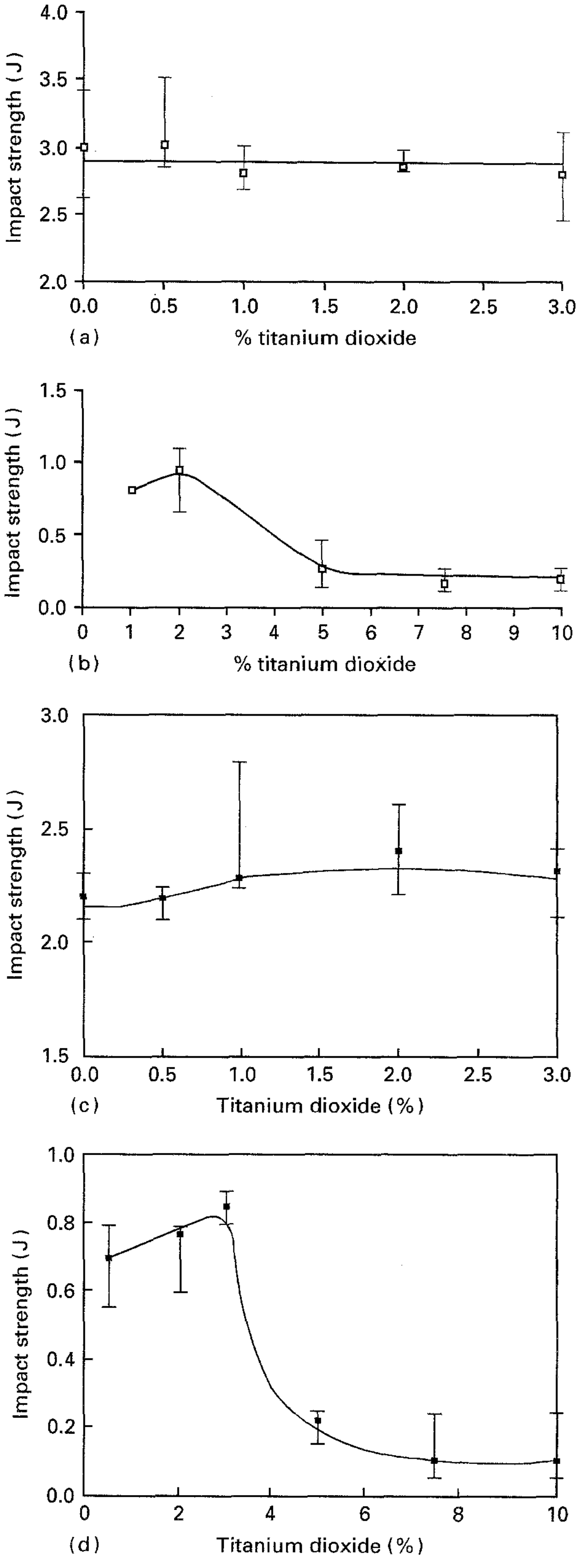

Figure 11 Impact strength of (a) ductile and (b) brittle failure dried PCD; (c) ductile and (d) brittle failure, PCA

3.3. Influence of filler materials on the molecular dynamics of the polymeric material

3.3.1. TSD measurements

The TSD spectra of the PCD samples are shown in Fig. 14. The incorporation of TiO_2 into the material leads to a slight lowering of the glass transition

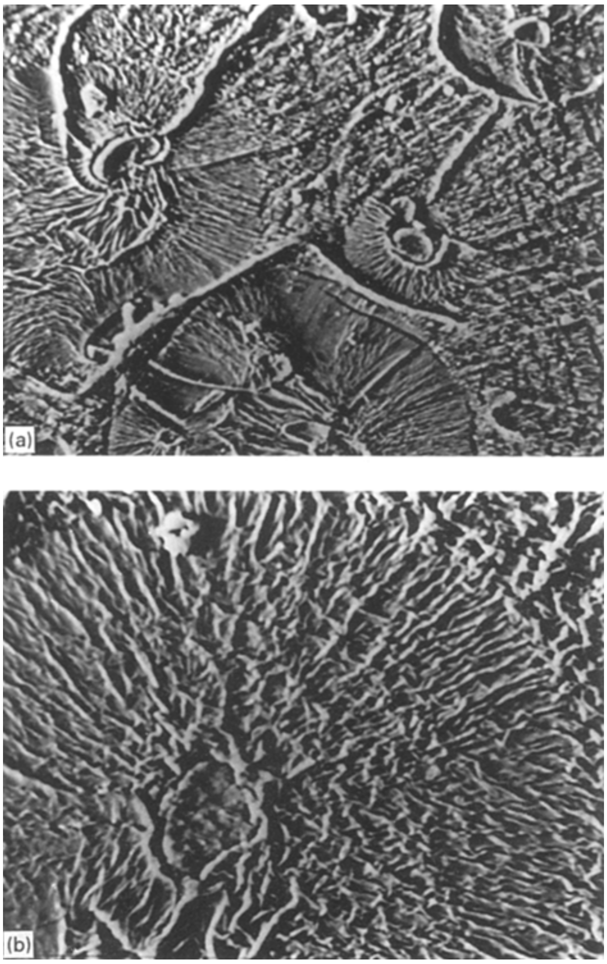

Figure 12 Brittle fracture surface: (a) × 160 magnification and (b) × 640 magnification.

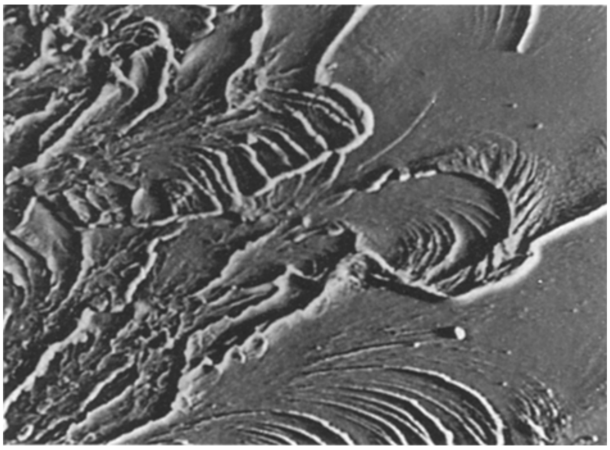

Figure 13 Ductile fracture surface, × 160 magnification.

temperature and also a diminution of the peak amplitude. Two features emerge from the variation of the TSD spectra with increasing levels of TiO_2. First, there is a decrease in the glass transition temperature and also a consequent decrease in the amplitude of the TSD peak associated with the dipolar relaxation process. Second, increasing the level of the pigment in the material leads to a situation where space charge hopping can occur between the particulate materials leading to the observation of a marked space charge peak above T_g. Increasing the filler level allows a percolation threshold to be achieved and a marked increase in the space charge peak amplitude. Similar behaviour was observed for the PCA samples. The effects are perhaps better shown in the area of the TSD peak, Fig. 15, which is associated with a drop in the number of dipoles orientating under the effects of the field; which in turn, is indicative of a restriction in the microchain movement and thus a lowering of the impact strength.

In summary, the TSD results can be explained in various ways. If water were playing a role in terms of plasticization–antiplasticization, then it is usual to observe antiplasticization at low levels and plasticization at high levels. This is a reverse of what is actually observed. This suggests that water does not play a major role in influencing the microscopic dynamics seen in these experiments. An alternative approach would be to suggest that the pigment nucleates the growth of crystallites which in turn leads to a reduction in the number of chains capable of executing local chain dynamics. This would suggest an increase in this effect with an increase in pigment loading, which is in line with other experimental observations.

3.3.2. Positronium lifetime measurements

The results of the positronium lifetime study of the filled polycarbonate are shown in Fig. 16a,b. Fig. 16a shows the liftime of the ortho positronium component. It is known that this lifetime is affected by the available free volume in a polymer matrix, but more specifically it is a probe for the volume of any voids within the matrix. The larger the volume the longer the ortho positronium lifetime. Fig. 16b shows the relative intensity of the ortho positronium lifetime component, again this is known to be affected by free volume, and the intensity of ortho positronium formation can be related to the concentration of voids within the matrix.

Initially both factors show an increase. This illustrates an increase in the free volume, and one would expect this to lead to an improvement in the mechanical response of the material. However, this increase is short lived and as pigment levels of greater than 2% are reached, the intensity of the ortho positronium component starts to fall off. When 5% loading level is reached the actual lifetime is also steadily reduced. However, the overall change in these values is only of the order of 5% and cannot be described as dramatic. Thus the loss of mechanical strength is not due to a large change in the overall free volume of the bulk matrix.

3.3.3. DSC results

The results for the two experiments carried out using DSC analysis are shown in Figs. 17 and 18.

Fig. 17 shows the variation in freezing point and melting point for pigmented PBT. One would expect the difference between these two temperatures to be reduced if the pigment materials were to act as nucleation sites for the solidification of the polymer. It can be

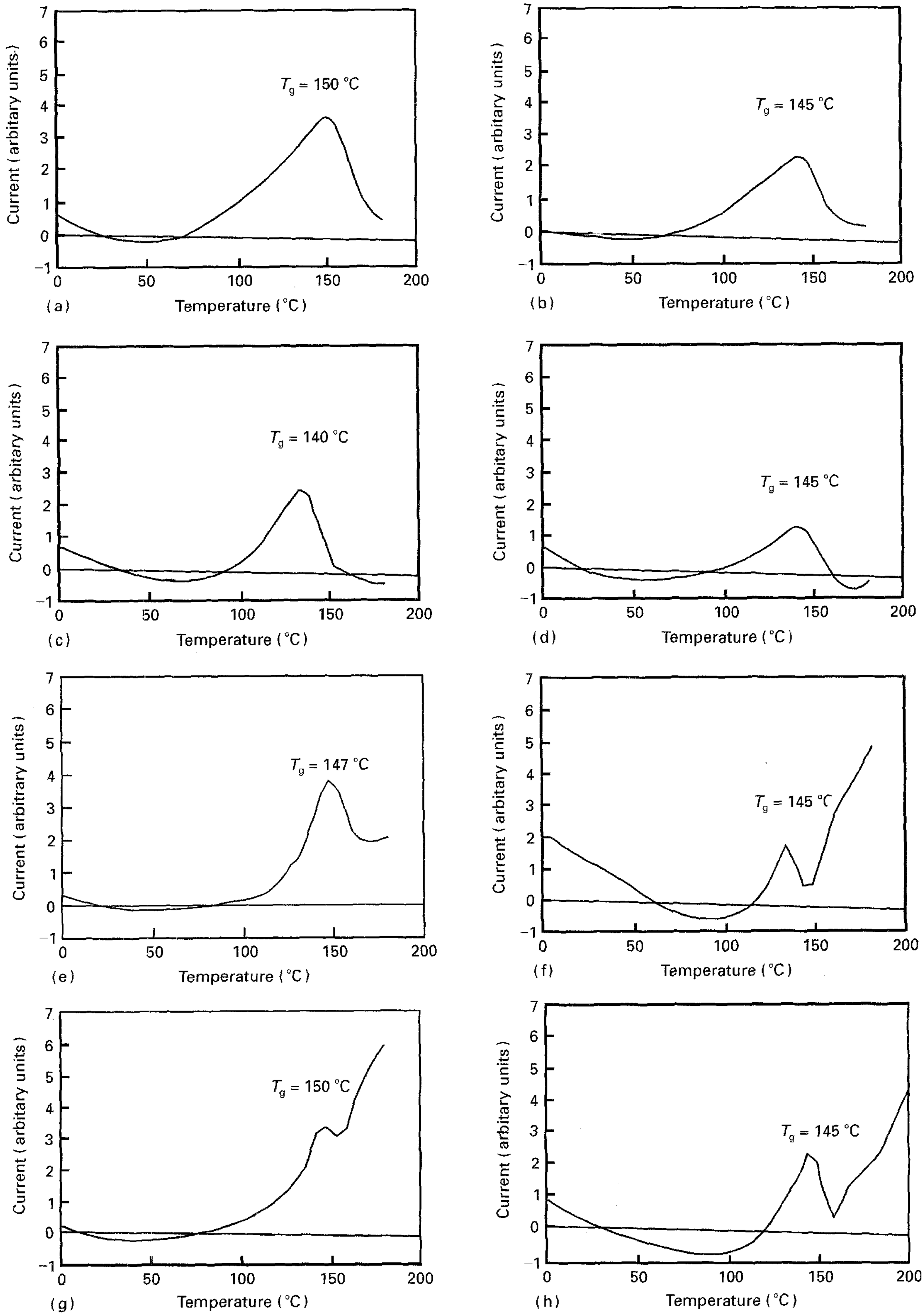

Figure 14 TSD spectra of dried PCD at pigment levels of: (a) 0%, (b) 0.5%, (c) 1%, (d) 2%, (e) 3%, (f) 5%, (g) 7.5% and (h) 10%.

seen from Fig. 17 that at the loading levels of pigment used, there was no evidence to suggest nucleation. However, it is difficult to draw a parallel with PC. PBT is a semicrystalline material, this allows one to analyse its melting and freezing temperatures, but PC is a generally amorphous polymer and as such may be more susceptible to the presence of nucleating sites. However, being amorphous it has no clearly defined melting or freezing temperature, and cannot therefore be analysed in the same way.

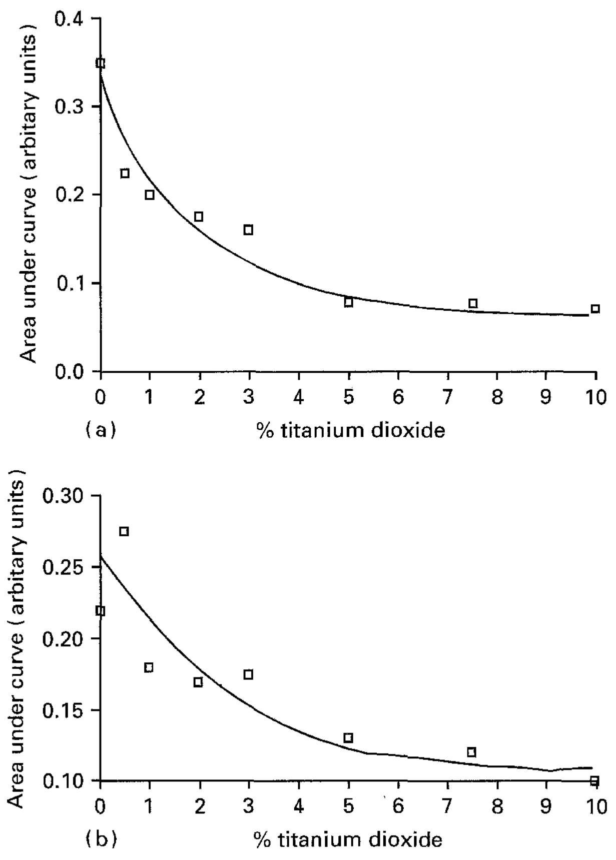

Figure 15 Area under the TSD peak versus pigment loading level.

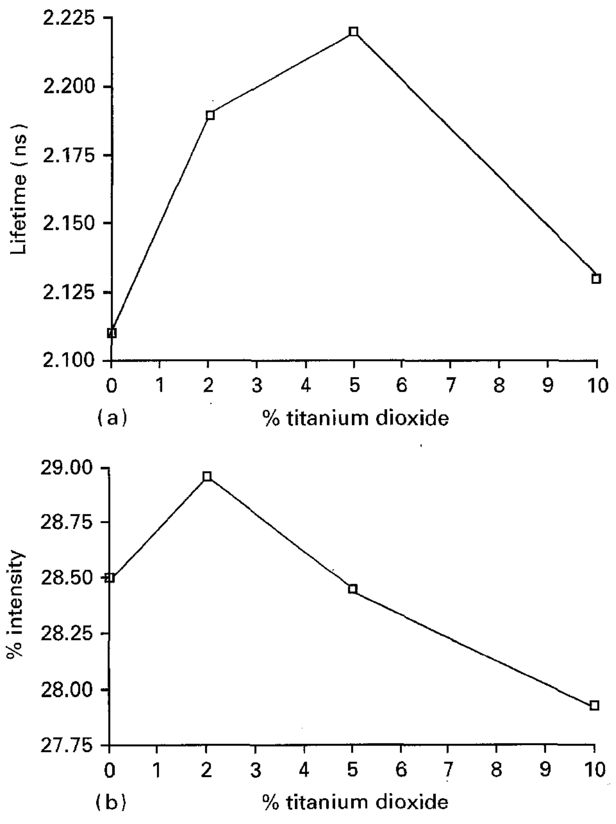

Figure 16 Positronium lifetime (a) and intensity (b) for pigmented PCD.

Fig. 18 shows the results for PC. There is a clear and steady decrease in the glass transition temperature with increasing pigment levels. This reinforces the evidence from the TSD results which also showed a decrease in glass transition temperature.

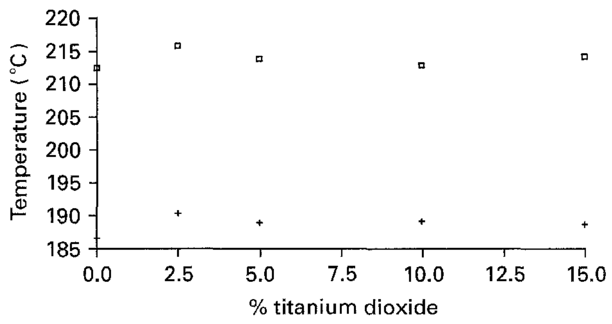

Figure 17 Melting (☐) and freezing (+) points for pigmented PBT.

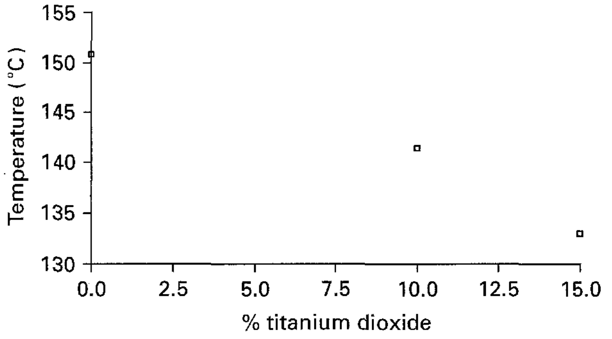

Figure 18 Effect of pigmentation on the T_g of PCD.

3.3.4. Dielectric results

In an attempt to show correlation between the TSD spectra of the authors materials and the microchain dynamics of the polymer, work was carried out using dielectric analysis of plasticized PC.

A recent paper by Liu et al. [29] had shown that the effect of filler material, in this case dibutyl phthalate (DBP), could be followed using nuclear magnetic resonance (NMR) studies. Liu illustrated that changes in the ability of microchain movements within PC, namely the so called “ring flip”, could be observed as being dependent upon the concentration of additive. The authors duplicated Liu’s materials and analysed them using dielectric spectroscopy. The results of these spectra confirmed Liu’s findings and in doing so gave a link between the microchain dynamics and the polarization mechanisms responsible for dielectric and TSD results.

4. Conclusions

From a comparison of the TSD, SEM and mechanical data one may draw the following conclusions. It appears that the incorporation of filler into the material leads to a densification of the polycarbonate around the filler particles. This process may be extremely localized and may not show up as a significant change in the bulk density of the material, or indeed as a dramatic change in the overall free volume of the sample. However, the ability of the material to undergo molecular reorientations may be radically altered and this will manifest itself as changes in the TSD spectra of the sample. This will in turn lead to a consequent reduction in the extent to which the polymer can exhibit local chain dynamics and, therefore, will introduce areas of lower energy dissipation when subjected to mechanical stress. The consequence of this is a tendency for the material to exhibit brittle failure and a low impact strength when subjected to loads at or near these weakened areas. The number and extent of these areas can be monitored using TSD techniques, as the concentration of these densified areas increases to a percolation threshold and there is the appearance of a space charge peak in the TSD spectrum. Clearly this densification process will depend critically on the processing conditions and hence the densification or otherwise around the particulate material may be a very subtle reflection of the conditions used in the processing. Other workers [30] have found similar effects to be induced by water absorption and have witnessed similar crater-like structures under SEM. This may suggest that the densification process is caused by water desorbtion from pigment agglomerates and is not merely due to their physical presence. However, the results from pigment dried at varying temperatures would suggest that varying the drying temperature does not radically alter the properties of the moulded specimen, but these results are by no means comprehensive and this topic certainly warrants further investigation.

The studies on PBT have proved to be rather inconclusive, this is compounded by the semicrystalline nature of this material making analysis results more difficult to interpret. However, the results for the low molecular weight PC demonstrate that this effect is not controlled by the polymer's molecular weight. Encapsulation of the filler proved to be futile and had no effect on the properties of the resulting material.

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